THE USE OF DICARBAMOYLSULFONATES AS TANNING AGENTS

Brian Milligan*

Commonwealth Scientific and Industrial Research Organization
Division of Protein Chemistry
Parkville (Melbourne), 3052
Victoria, Australia

and

Peter R. Buechler

Eastern Regional Research Center
600 E. Mermaid Lane
Philadelphia, Pennsylvania 19118

Abstract

Four water-soluble crosslinking agents have been examined as tanning agents for sheepskin and cattlehide. Three were dicarbamoylsulfonates made by bisulfite addition to diisocyanates, the fourth was terephthaloyl thiosulfate. All four were tested as primary tannages, and the bisulfite adducts were also used to retan slack chrome- and zirconium-tanned leathers.

Each of the bisulfite adducts tanned the hides and skins, as shown by an increase in shrinkage temperature and resistance to enzymic digestion, but subjective and mechanical testing revealed various deficiencies in the resultant leathers. Terephthaloyl thiosulfate had little tanning action.

Better results were obtained using the bisulfite adducts as retanning agents. In particular, retannage with the bisulfite adduct of tolylene diisocyanate greatly improved the fullness, resilience, flexibility, break, color, thermal stability, and enzymic resistance of chrome-tanned leather, with minimal effects on other desirable properties.

vironmental regulations requiring the removal of all but traces of chromium from tannery wastes and a predicted world-wide shortage of chromium, have prompted this search for alternative tanning agents. One possibility is to develop tanning agents capable of replacing chromium entirely, while another is to find retanning agents which would lessen the amount of chrome required for tanning initially.

There are hundreds of bifunctional organic compounds that are capable of introducing covalent crosslinks into collagen and therefore have the potential to serve as tanning agents. However, only two covalent crosslinking agents, formaldehyde and glutaraldehyde, have seen significant industrial use (1-3). The unique combination of properties that results from successful tannage obviously requires much more than the simple introduction of crosslinks. Probably the number, size, and location of the crosslinks, as well as any change in the electrostatic charge and hydrophilic/hydrophobic character of the collagen, all play a part of determining the properties of the resultant leather.

Diisocyanates have been used to tan leather by the introduction of covalent crosslinks. This tannage has been carried out both in anhydrous organic solutions (4) and in aqueous emulsions (5, 6). Disadvantages which have prevented commercial adoption include the toxicity of isocyanates, the use of organic solvent, or the loss of tanning agent by competitive hydrolysis during aqueous treatment.

Petersen (7) has described a method of forming carbamoylsulfonate ion by reaction of an isocyanate with bisulfite ion.

$$RN=C=O \;+\; HSO_3^- \longrightarrow RN-\overset{\overset{\textstyle O}{\|}}{\underset{}{C}}-SO_3^- $$
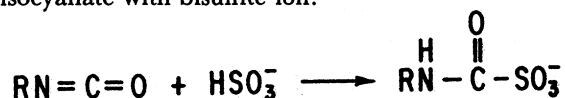
If the bisulfite ion is accompanied by a highly solubilizing cation, e.g., in the case of sodium bisulfite, a soluble carbamoylsulfonate salt is formed:

$$RNCO \;+\; NaHSO_3 \longrightarrow RNHCOSO_3^- + Na^+$$

The main tanning agents used in the work described in the present paper are these soluble carbamoylsulfonates. The carbamoylsulfonates are not only water-soluble, but they are also reasonably resistant to hydrolysis in neutral and acid solutions in contrast to the parent isocyanates.

Carbamoylsulfonates, like the parent isocyanates, react with amines to give ureides (7):

$$RNHCOSO_3Na \;+\; R'NH_2 \longrightarrow RNHCONHR' + NaHSO_3$$

Therefore dicarbamoylsulfonates should introduce crosslinks between amino-terminated side-chains in collagen, and thus function as tanning agents. In contrast to diisocyanates, they should be applicable from aqueous solution with minimal risk of hydrolysis. There is already indirect evidence that they can crosslink collagen, since they are used to thicken gelatin solutions (8) and to strengthen cat-

gut sutures (9). Cater (10) tested dicarbamoylsulfonates made from tolylene diisocyanate and hexamethylene diisocyanate as tanning agents in 1955, but found that relatively few crosslinks were introduced. However, the reactions were performed in acid medium where presumably the terminal amino groups were in the ionic rather than the reactive amine form. Dicarbamoylsulfonates, in conjunction with diamines and other curing agents, have also been examined as water-based finishing treatments for leather.*

The dicarbamoylsulfonates examined as tanning agents in this paper were prepared from tolylene diisocyanate (TDI), hexamethylene diisocyanate (HMDI), and isophorone diisocyanate (IPDI). The dicarbamoylsulfonates of these isocyanates were prepared by reaction with bisulfite (7) and they will therefore be referred to hereafter as "bisulfite adducts."

In addition to these bisulfite adducts, a second type of potential tanning agent, terephthaloyl thiosulfate (TPTS), was also prepared and tested as part of this work. Acyl thiosulfates are water-soluble acylating agents which react readily with amines, phenols, and alcohols in aqueous solution (11). Bifunctional analogues like TPTS (see formula) therefore have the potential for crosslinking and tanning collagen. The structures of the three bisulfite adducts and terephthaloyl thiosulfate, identified by their abbreviated symbols, are as follows:

TDI.BA

$KO_3SCONH(CH_2)_6NHCOSO_3K$

HMDI.BA

IPDI.BA

NaO_3SSCO—⟨O⟩—$COSSO_3Na$

TPTS
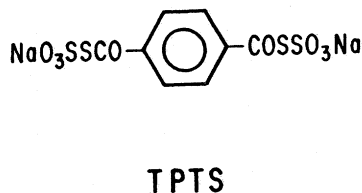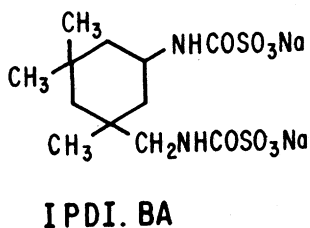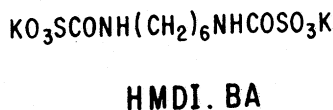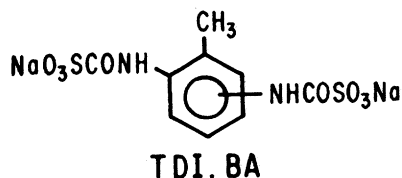
The bisulfite adduct of phenyl isocyanate (PI · BA) was also used as a monofunctional "control" reagent for comparison with TDI.BA.

It may not be good practice to refer to a compound by its method of preparation, since alternate synthetic routes to the same compound may become available. Nevertheless, this practice will be adopted in this paper for a number of reasons: (1) It identifies the isocyanate from which it was made, (2) it permits easy comparison with the analogous reactions carried out in organic media with

isocyanates, and (3) it provides a simple shorthand symbolism for these adducts based on the one already known that was developed for the isocyanates.

Experimental

MATERIALS* AND METHODS

Hides. The pickled New Zealand sheepskins were a gift from John Flynn and Sons, Salem, MA.† They were degreased with kerosene, rinsed with 6 percent sodium chloride solution, and stored at 4°C before use. The Hereford cattle hides were unhaired, limed, split (to 9 oz), delimed, bated and pickled, and stored in the pickle liquor (pH 2.2) before use.

Reagents. Tanolin R (Hamblet and Hayes Co.), Zircotan 33 (Rohm and Haas), and solvent fatliquor XS76-31 (Reilly-Whiteman Inc.) were kindly donated by the manufacturers.

Bisulfite Adducts. Phenyl isocyanate (Aldrich Chemical Co.), hexamethylene diisocyanate (Columbia Organic Chemicals Co.), and tolylene diisocyanate (a mixture containing 80 percent of the 2,4-isomer and 20 percent of the 2,6-isomer, from Allied Chemical Corp.) were converted to their bisulfite adducts by the methods described by Maclaren and coworkers (12, 13).

Isophorone diisocyanate (Thorson Chemical Corp.) was converted to its bisulfite adduct by stirring a solution of the diisocyanate (67 g) in dioxane (120 ml) with an aqueous solution (180 ml) of sodium metabisulfite (63 g) at 30°C for 2 days. Addition of ethanol (3 l.) to the resultant homogeneous solution precipitated the bisulfite adduct, which was collected, washed with ethanol, and dried *in vacuo*.

The yields and purity of the bisulfite adducts are shown in Table I.

TABLE I

YIELDS AND PURITY OF BISULFITE ADDUCTS OF DIFFERENT ISOCYANATES

Isocyanate	Bisulfite adduct	Yield	Purity[a]
		%	%
Phenyl isocyanate	PI.BA	66	89
Tolylene diisocyanate	TDI.BA	87	88
Hexamethylene diisocyanate	HMDI.BA	79	95
Isophorone diisocyanate	IPDI.BA	88	86

[a]Determined by iodimetric titration (13).

* A number of chemical compounds are described in this paper, some of which (e.g., the isocyanate compounds) have hazardous properties. Material safety data sheets on all chemicals employed should be obtained from the manufacturers and their recommendations for safe use should be followed. The dicarbamoylsulfonates and the terephthaloyl thiosulfate prepared in this paper are new chemicals and their toxicities have yet to be determined. Therefore, the usual precautions of technically competent supervision and care in handling of new materials should be followed.

† Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

Terephthaloyl thiosulfate. A solution of terephthaloyl chloride (Aldrich Chemical Co., 10.0 g) in dioxane (50 ml) was added dropwise over 10 min to a magnetically stirred aqueous solution (50 ml) of sodium thiosulfate pentahydrate (25.0 g) at 20 to 25°C. After stirring for a further 30 min, the mixture was cooled at 5°C, and the product was filtered off, washed with cold water and acetone, and dried *in vacuo.* TPTS was obtained as colorless needles in 94 percent yield. Treatment with an excess of aniline in aqueous solution at 20°C for 1 hr gave the corresponding dianilide (87 percent), mp 350 to 353°C. Addition of excess sodium hydroxide solution to the TPTS resulted in immediate hydrolysis, liberating thiosulfate ion in 97 percent yield.

Treatments. Hide samples (usually 30 cm × 30 cm) were treated at room temperature in 1.8-1. jars tumbled at a rate of 40 rpm. Pickled hide was used directly for chrome or zirconium tannage, but was adjusted to pH 4 to 5 before the organic tanning agents were applied. The amounts of materials used for treatment are expressed as percentages of the original pickled stock weight.

Chrome Tannage. The pickled stock was tumbled for 1 hr with sodium chloride (4 percent), sodium formate (0.5 percent), and sufficient sulfuric acid in water (100 percent) to adjust the liquor to pH 1.8. A cooled solution of Tanolin R (4 to 8 percent), previously made up in boiling water (70 percent), was then added, and tumbling continued for 3 to 4 hr. Aliquots of an aqueous solution of sodium bicarbonate (0.5 percent) were next added at 30-min intervals until the liquor reached and maintained pH 4.0.

Zirconium Tannage. The pickled stock was tumbled with sodium chloride (10 percent) in water (150 percent) for 20 min, after which solid Zircotan 33 (10 percent) was added, followed after 3 hr by a slurry of calcium hydroxide (2 percent). One hour later aliquots of sodium bicarbonate (0.5 percent) were added at 30-min intervals until the liquor reached and maintained pH 3.8.

Tannage with Bisulfite Adducts. Pickled stock (adjusted to pH 4 to 5) or slack-tanned leather was tumbled for 30 min with the appropriate bisulfite adduct (10 to 20 percent) in water (100 percent). In the case of TDI.BA or PI.BA, aliquots of an aqueous solution of sodium bicarbonate (0.5 to 1.0 percent) were then added at 15-20 min intervals until pH 7.0 was reached (about 2 hr), followed by aliquots of sodium carbonate solution (0.3 to 0.6 percent) until the liquor reached and maintained pH 8.0. Excessive foaming was inhibited by adding Antifoam GC (Laurel Products Corp.). When using HMDI.BA or IPDI.BA, aliquots of sodium carbonate solution (0.5 to 1.0 percent) were added at 15-to-20-min intervals throughout, until the liquor maintained pH 9.0. Treatment was continued until iodimetric titration of a portion of the liquor showed that 90 to 95 percent of the bisulfite adduct had reacted. About 5 hr was usually required for tannage. At this stage the leather was rinsed, adjusted to pH 4 to 5 by tumbling in dilute acetic acid, and rinsed again. Part of the sample was dried for analysis, and the remainder was fatliquored (see below).

Tannage with Terephthaloyl Thiosulfate (TPTS). Pickled sheepskin was adjusted to pH 4, rinsed, and tumbled with a suspension of TPTS (20 percent) in water (200 percent). After 30 min aliquots of sodium bicarbonate (1.0 percent) were added at 15 min intervals until the tanning agent had completely dissolved and the liquor had reached pH 6.

Fatliquoring, Samming, and Staking. All leather samples were adjusted to pH 4 to 5, rinsed, drained, and then tumbled (initially at 40°C) with solvent fatliquor (5 percent) in water (100 to 150 percent) for 1 to 2 hr. They were then rinsed briefly, set out, and allowed to dry at room temperature. Water (35 percent) was added to the dry samples which were stored in plastic bags overnight and then staked by hand (sheepskin) or mechanically (cattlehide).

Shrinkage Temperatures. A Theis shrinkage meter was used to measure the shrinkage temperature of strips of wet leather taken prior to fatliquoring.

Enzymic Digestibility. Tanned sheepskin samples (prior to fatliquoring) and de-pickled sheepskin (as a control) were finely powdered in a Wiley mill (3 passes, #10 mesh). Weighed samples (*ca* 25 mg) of known moisture content were shaken at 38°C with: 1) a 0.1 percent solution of trypsin (Calbiochem) in 0.1 M $NaHCO_3$, 2) a 0.1 percent solution of pepsin (Nutritional Biochemicals Corp.) in 0.2 M HCl, or 3) a 0.1 percent solution of Pronase (Calbiochem) in 0.05 percent borate buffer (pH 8.0). Enzyme solutions were also incubated alone to permit correction of the results for autolysis. After incubation for 18 hr, the samples were diluted with water (18.0 ml), filtered, and aliquots (0.2 or 0.4 ml) analyzed for their peptide content with ninhydrin reagent. The resultant purple solutions were analyzed with a Beckman DB spectrophotometer at 570 nm, and the enzymic digestibility of the various samples was calculated as a percentage of that of depickled sheepskin.

Consumption of Bisulfite Adducts During Tanning. Iodimetric analysis was used to estimate both the amount of bisulfite adduct sorbed from solution by collagen, and the extent to which it had reacted covalently. The bisulfite adducts contained small amounts of bisulfite ion (< 2 percent) as contaminants. Additional bisulfite ion arises as the result of either hydrolysis of the adduct or covalent reaction with functional groups in the collagen. Iodimetric titration of an aliquot of the tanning liquor permits calculation of the level of contamination, and of the amounts of bisulfite formed as tannage proceeds. Residual bisulfite adduct in the solution can then be quantitatively converted to bisulfite by addition of alkali, and also estimated iodimetrically (13).

Weight increases due to tannage with TDI.BA were determined by comparison of the amino acid contents of the tanned sheepskin samples with that of depickled sheepskin. The powdered samples were hydrolyzed with 6 M HCl at 106°C for 18 hr, and the total amino acid contents then determined by a colorimetric ninhydrin procedure. The procedure was unsuitable for analysis of leather tanned with the bisulfite adducts of aliphatic diisocyanates because they give ninhydrin-positive diamines on hydrolysis.

Determination of Physical Properties. Tensile strengths were determined with an Instron tensile tester (model TTB) according to ASTM D-2209-64 on leather strips cut parallel to the backbone. The samples were conditioned at 22°C and 51 percent RH for 48 hr before measurement.

Ball bursting strength was obtained according to ASTM D-2207-64 and grain crack data on a Satra Lastometer apparatus according to SLP-9 (IUP/9).

Torsional moduli were determined according to ASTM D-2821-72, using a Williamson type semi-automatic wire stiffness tester (14).

Results and Discussion

TANNAGE WITH BISULFITE ADDUCTS ALONE. Preliminary experiments on the uptake of the bisulfite adduct of tolylene diisocyanate (TDI.BA) from weakly acidic solutions by sheepskin showed that an appreciable fraction was sorbed. Equilibrium uptake was reached within 30 min. More of the bisulfite adduct was sorbed at pH 3.5 than at pH 5.0; the amount sorbed also increased with increasing initial concentration (See Table II). This behavior suggests that only ionic binding oc-

TABLE II

EXTENT OF UPTAKE[a] OF TDI.BA FROM ACID SOLUTIONS
BY DEPICKLED SHEEPSKIN[b]

Initial conc. (M)	pH	Equilibrium conc. (M)	Extent of uptake[c]
			%
0.118	3.5	0.060	49
0.236	3.5	0.137	43
0.472	3.5	0.307	35
0.236	5.0	0.165	30
0.472	5.0	0.354	25

[a] Determined spectrophotometrically at 235 nm.
[b] After 30 min, using a 200 percent float.
[c] As a percentage of the amount of bisulfite adduct offered.

curs under these conditions, a conclusion confirmed by iodimetric titration which showed that no bisulfite was released during binding. Any covalent reaction between the bisulfite adduct and amino or hydroxyl groups in the collagen would have released bisulfite ions into the solution.

The above treatments caused no significant increase in shrinkage temperature of sheepskin, a result consistent with the absence of covalent cross-linking. Cater (10) used similar conditions for treating kangaroo tail tendons with bisulfite adducts, and it is therefore not surprising that he observed relatively small increases in shrinkage temperature.

However, covalent reaction of bisulfite adducts with collagen can be induced

by gradual addition of alkali. The bisulfite adducts of aromatic isocyanates are more reactive than those of aliphatic isocyanates, the former reacting covalently with collagen at pH 6 to 8, whereas the latter require pH 8 to 9. The extent of reaction can be readily followed by iodimetric titration of the bisulfite ion liberated. Addition of alkali must be gradual to avoid hydrolysis of bisulfite adducts, the products of which result in the deposition of insoluble polyureas.

As shown in Table III, application of the bisulfite adduct of a diisocyanate to sheepskin with gradual addition of alkali results in a substantial increase in shrinkage temperature. Treatment with TDI.BA produced the largest increase

TABLE III

EFFECT OF VARIOUS TANNING AGENTS ON THE SHRINKAGE TEMPERATURE, THICKNESS, AND ENZYMIC DIGESTIBILITY OF SHEEPSKIN

Reagent	Amount offered[a]	Ts	Thickness	Enzymic digestibility[b]		
				Pronase	Pepsin	Trypsin
	%	°C	mm	%	%	%
—	—	59	0.28	100	100	100
TDI.BA	20	88	1.03	9	1	0
PI.BA	12.5	62	0.56	85	65	98
HMDI.BA	20	69	0.50	24	24	4
IPDI.BA	20	72	0.74	8	6	0
TPTS	20	65	0.41	107	82	80
Tanolin R	8	98	0.95	61	34	28

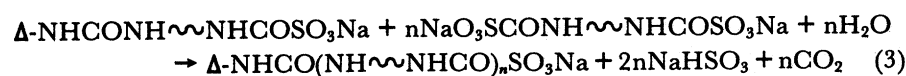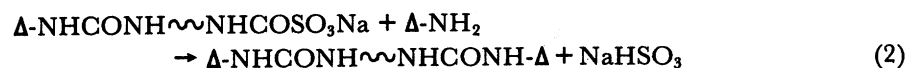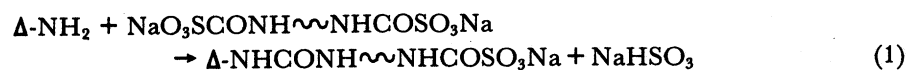[a] As a percentage of the pickled sheepskin weight.
[b] As a percentage of the enzymic digestibility of depickled sheepskin.

(29°C) in shrinkage temperature and in leather thickness; values for chrome-tanned sheepskin are included in the table for comparison. By contrast, application of the bisulfite adduct of phenyl isocyanate (PI.BA), a monofunctional analogue of TDI.BA (and therefore incapable of introducing crosslinks), caused little increase in shrinkage temperature.

Resistance to proteolytic enzymes is sometimes used to assess the effectiveness of a tanning agent (15), as it estimates leather's ability to withstand bacterial deterioration under damp or wet conditions. The results in Table III show that tannages with the bisulfite adducts of the three diisocyanates confer excellent resistance to digestion by the enzymes pronase, pepsin, and trypsin. These leather samples are considerably more resistant to proteolytic digestion than the conventionally chrome-tanned sample. Comparison of the results for TDI.BA and the monofunctional "control" reagent, PI.BA, indicates that the protective effect of the former is most likely due to its ability to crosslink collagen.

Treatment of sheepskin with TPTS, a different class of crosslinking agent, caused only a small increase in shrinkage temperature, and gave a thin, papery leather with little resistance to proteolytic enzymes (see Table III). These results indicate that TPTS introduces few crosslinks into collagen.

Bisulfite adducts, like their parent isocyanates, react with a variety of functional groups in proteins (16, 17), and the use of diisocyanate derivatives further increases the number of possible reactions. However, there is little doubt that the main sites of attack are the amino groups of lysine, hydroxylysine, and histidine residues. The following equations show four possible reactions of the bisulfite adduct of a diisocyanate with an amine. Reaction via equations 1 and 2 give rise to simple crosslink formation, while reactions as shown in equation 3 can eventually lead to polymeric crosslinks (equation 4).

$$\Delta\text{-}NH_2 + NaO_3SCONH\sim\sim NHCOSO_3Na$$
$$\rightarrow \Delta\text{-}NHCONH\sim\sim NHCOSO_3Na + NaHSO_3 \tag{1}$$

$$\Delta\text{-}NHCONH\sim\sim NHCOSO_3Na + \Delta\text{-}NH_2$$
$$\rightarrow \Delta\text{-}NHCONH\sim\sim NHCONH\text{-}\Delta + NaHSO_3 \tag{2}$$

$$\Delta\text{-}NHCONH\sim\sim NHCOSO_3Na + nNaO_3SCONH\sim\sim NHCOSO_3Na + nH_2O$$
$$\rightarrow \Delta\text{-}NHCO(NH\sim\sim NHCO)_nSO_3Na + 2nNaHSO_3 + nCO_2 \tag{3}$$

$$\Delta\text{-}NHCO(NH\sim\sim NHCO)_nSO_3Na + \Delta\text{-}NH_2$$
$$\rightarrow \Delta\text{-}NHCO(NH\sim\sim NHCO)_nNH\text{-}\Delta + NaHSO_3 \tag{4}$$

Similar reactions, involving the hydroxyl groups of serine, threonine, hydroxyproline, and hydroxylysine residues or the phenolic group of a tyrosine residue, may also occur, although less readily than those with amino groups. Large weight increases (up to 20 percent on a dry weight basis) are observed on treating sheepskin with bisulfite adducts of diisocyanates. These large amounts can be accounted for only by invoking the introduction of polymeric species (equations 3 and 4), or extensive reaction with hydroxyl groups as well as with amino groups. The formation of polymeric species seems the more likely explanation.

Although shrinkage temperature and enzymic digestion determinations indicate that bisulfite adducts of diisocyanates (especially TDI.BA) may be useful tanning agents, subjective and physical testing shows that the resultant leather suffers from various deficiencies. Among these are stiffness and proneness to grain crack, as shown in Table IV. The leather has a good white color, but its grain shows poor break. Leather tanned with TDI.BA has better physical properties, but is more subject to grain crack and shows poorer break than chrometanned sheepskin. It is cream in color, and has satisfactory temper and flexibility. Of the three bisulfite adducts tested, TDI.BA shows most promise as a primary tanning agent, but it is not entirely satisfactory.

Application of the bisulfite adducts to cattlehide gave similar results to those obtained using sheepskin (see Table V). Again, TDI.BA gave the fullest, most flexible leather, but the grain showed poor break in comparison with a chrometanned control. None of the cattlehide samples, including the control, was well-

TABLE IV

PHYSICAL PROPERTIES OF LEATHER PRODUCED BY TANNING SHEEPSKIN WITH DIFFERENT TANNING AGENTS

Tanning agent[a]	Apparent density	Load to break	Tensile strength	Ball-burst strength	Grain-crack load	Torsional modulus
	g/cm^3	kg	kg/cm^2	kg/cm^2	kg	kg/cm^2
TDI.BA	0.454	21.0	161	99	18.5	368
HMDI.BA	0.584	14.6	238	190	6.3	4246
IPDI.BA	0.431	14.2	153	92	3.0	1603
TPTS	0.588	17.9	313	231	16.7	4036
Tanolin R	0.453	20.5	162	153	25.7	305

[a] 20 percent on pickled weight for the organic tanning agents, 8 percent for Tanolin R.

TABLE V

PROPERTIES OF LEATHER PRODUCED FROM CATTLEHIDE WITH DIFFERENT TANNING AGENTS[a]

Reagent	Ts[b]	Thickness	Resilience	Flexibility	Break
	°C	mm			
TDI.BA	74	2.57	too high	satis.	poor
HMDI.BA	64	1.68	too high	poor	fair
IPDI.BA	69	1.68	too high	poor	fair
Tanolin R	80	2.44	good	good	satis.

[a] Using 20 percent of the bisulfite adducts and 8 percent of Tanolin R, based on pickled weight.
[b] The depickled hide had a shrinkage temperature of 54 to 55°C.

tanned, probably due to the failure of the samples to tumble and flex during treatment.

RETANNAGE WITH BISULFITE ADDUCTS.

On the basis of the above results it seems unlikely that bisulfite adducts will be useful as primary tanning agents. However, they could serve as retanning agents for slack-tanned leather, thus reducing the amount of chrome required for the initial tannage. Tanning with lower levels of chrome may also result in better exhaustion of the chrome liquors. Moreover, leather retanned with bisulfite adducts would be expected to be more durable to wet treatments than that retanned with vegetable tannins or syntans, which are not covalently bound by the leather.

RETANNAGE OF CHROME-TANNED LEATHER.

As seen from the results in Table VI, retannage of slack chrome-tanned sheepskin with TDI.BA results in a marked increase in leather thickness, thermal stability, and enzymic resistance; the initial grey-green color of the grain is also changed to a more desirable cream color.

Retannage with IPDI.BA gives a white, full leather with good enzymic resistance, but in this case there is no increase in thermal stability (see Table VI). This

TABLE VI

CHANGES IN SHRINKAGE TEMPERATURE, THICKNESS, AND ENZYMIC DIGESTIBILITY CAUSED BY RETANNING CHROME- OR ZIRCONIUM-TANNED SHEEPSKIN WITH BISULFITE ADDUCTS

First tannage		Retannage			Enzymic digestibility[a]		
Reagent	Ts	Reagent	Ts	Thickness	Pronase	Pepsin	Trypsin
	°C		°C	mm	%	%	%
Run 1							
Tanolin R (4%)	94	—	94	0.82	45	24	38
"	94	TDI.BA (10%)	100 (3 min)	1.00	7	6	0
"	94	TDI.BA (20%)	100 (15 min)	1.04	2	0	0
Run 2							
Tanolin R (4%)	89	—	89	0.94	64	58	79
"	89	IPDI.BA (20%)	88	1.39	5	7	2
Run 3							
Zircotan 33 (10%)	82	—	82	0.99	57	0	119
"	82	TDI.BA (20%)	89	1.00	6	0	0

[a] As a percentage of the enzymic digestibility of depickled sheepskin.

last result is attributable to a change in the nature of binding of the chrome, induced by the high pH (9.0) required for retannage (18). Treatment of slack chrome-tanned sheepskin under the conditions used for retannage, with omission of the bisulfite adduct, reduces the shrinkage temperature from 89°C to 77°C.

Determination of physical properties (see Table VII) showed that retannage of chrome-tanned sheepskin with bisulfite adducts effects a marked reduction in apparent density and stiffness (torsional modulus), with little change in tensile

TABLE VII

CHANGES IN PHYSICAL PROPERTIES CAUSED BY RETANNING SLACK CHROME-TANNED OR ZIRCONIUM-TANNED SHEEPSKIN WITH BISULFITE ADDUCTS

First tannage	Retannage	Apparent density	Load to break	Tensile strength	Ball-burst strength	Grain-crack load	Torsional modulus
		g/cm^3	Kg	Kg/cm^2	Kg/cm^2	Kg	Kg/cm^2
Tanolin R (4%)	—	0.479	22.7	157	146	24.8	396
"	TDI.BA (10%)	0.395	19.1	143	100	15.3	151
"	TDI.BA (20%)	0.389	21.5	161	108	16.0	165
"	IPDI.BA (20%)	0.399	22.4	125	106	22.7	110
Zircotan 33 (10%)	—	0.467	23.5	197	135	26.3	185
"	TDI.BA (20%)	0.516	25.8	191	145	22.0	413

strength. However, there is some reduction in ball-burst strength and grain-crack load. There seems to be little advantage in using more than 10 percent of TDI.BA, based on the original pickled weight of the skin.

Retannage of chrome-tanned side leather with TDI.BA or IPDI.BA gave similar results to those obtained with sheepskin (see Table VIII). The best leather

TABLE VIII

SUBJECTIVE ASSESSMENT OF PROPERTIES OF SLACK CHROME-TANNED
CATTLE HIDE[a] BEFORE AND AFTER RETANNAGE WITH BISULFITE ADDUCTS

Retannage	T_s	Resilience	Flexibility	Fullness	Break	Color
	°C					
–	74	insuff.	satis.	poor	fair	gray
TDI.BA (10%)	84	v. good	v. good	fair	good	cream
TDI.BA (20%)	85	good	good	good	good	cream
IPDI.BA (20%)	77	excessive	satis.	good	v. good	white

[a] Tanned with 4% Tanolin R, based on pickled weight.

was produced by retannage with TDI.BA (10 percent). This treatment greatly improved the resilience, temper, flexibility, fullness, break, and color of the original leather. Excellent results were also obtained when tannage was carried out on a larger scale, using a pickled side in a 6-ft. diameter drum. Primary tannage with Tanolin R (5 per cent), followed by retannage with TDI.BA (10 percent), gave very good leather.

Experiments in which sheepskin was first tanned with bisulfite adducts and then retanned with chromium salts were technically inconvenient, due to the major adjustments in pH required, and gave very stiff, unacceptable leather.

RETANNAGE OF ZIRCONIUM-TANNED LEATHER. The successful use of bisulfite adducts for retanning chrome leather prompted us to explore their use on zirconium-tanned sheepskin. As the results in Table VI show, retannage with TDI.BA increased the shrinkage temperature and resistance to proteolytic enzymes, but produced no increase in leather thickness. Measurement of other properties (see Table VII) showed that the major changes due to retannage were an increase in apparent density and in stiffness. Other treatments of zirconium-tanned leather with bisulfite adducts caused a decrease in shrinkage temperature. Unfortunately, zirconium-tanned leather is even more susceptible to alkali than chrome-tanned leather, and appreciable loss of tannage occurs, even at pH 8. This sensitivity to alkali probably precludes the use of bisulfite adducts for retanning zirconium-tanned leather.

Concluding Remarks

Bisulfite adducts of diisocyanates show most promise as retanning agents for chrome leather, TDI.BA giving best results of the three adducts studied. It greatly

improves the fullness, resilience, temper, flexibility, break, color, and enzymic resistance of chrome-leather. However much more work is required to establish whether bisulfite adducts would be useful retanning agents for industrial use. The adducts are not commercially available, but they are easy to prepare from their readily available parent diisocyanates.

Disadvantages of bisulfite adducts for retanning include the need to make frequent and gradual additions of alkali during application, and to lower the pH of the retanned leather before fatliquor can be applied. Leather retanned with TDI.BA also discolors rapidly in sunlight. The IPDI.BA retannage does not suffer from this defect, but requires a higher pH, which may modify the primary mineral tannage. Despite these disadvantages, bisulfite adducts of diisocyanates show sufficient merit as retanning agents to warrant more detailed investigations.

Acknowledgements

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